

## ALD Capping Layers for Superconducting Radio Frequency Accelerator Cavities

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Superconducting radio frequency (SCRF) materials are becoming increasingly important for a variety of applications. Applications range from cellular phone networks to high energy physics particle accelerators such as the International Linear Collider (ILC). Improvement of these devices requires coherent, high purity surface films of nanometer thickness. Here Atomic Layer Deposition (ALD) methods are described for producing well defined dielectric (Al<sub>2</sub>O<sub>3</sub>) films on Nb, the substrate of choice for SCRF applications.

### Introduction

Atomic layer deposition (ALD) is a thin film growth method using alternating, self limiting reactions between gaseous precursors and a solid surface to deposit materials in an atomic layer-by-layer fashion[1]. These attributes allow highly conformal and uniform films with atomically abrupt interfaces to be deposited on complex, 3-dimensional substrates such as aerogels[2], powders[3], and anodic aluminum oxide (AAO) membranes[4]. These attributes make ALD an ideal synthesis method for modifying SCRF cavities for particle accelerator applications. The layout of the proposed International Linear Collider (ILC) for instance includes many kilometers of superconducting Nb cavities held at >2 K in ultrahigh vacuum (UHV). The purity of the interior surfaces of these Nb cavities are crucial[5] because for SCRF applications these surfaces carry all of the considerable electrical current needed to drive ions with acceleration gradients exceeding 35 MV/m. The cavities themselves are complex in shape and require the unique 3-dimensional coating capability offered by the ALD method.

Nb is generally accepted as the best material for SCRF cavities. It has been chosen because it has the highest lower critical field temperature of any known superconductor. For type 2 superconductors, the lower critical field temperature is the phase transition temperature below which the material becomes truly resistance free. Because cooling these cavities is both difficult and expensive, even the slight resistance found above this temperature is unacceptable. Unfortunately, Nb is chemically labile, forming significant oxide layers even in UHV conditions. Moreover, the oxide is compositionally complex, forming identifiable phases ranging from Nb<sub>2</sub>O<sub>5</sub> to Nb<sub>2</sub>O with properties that range from superconducting oxides to strict dielectrics.

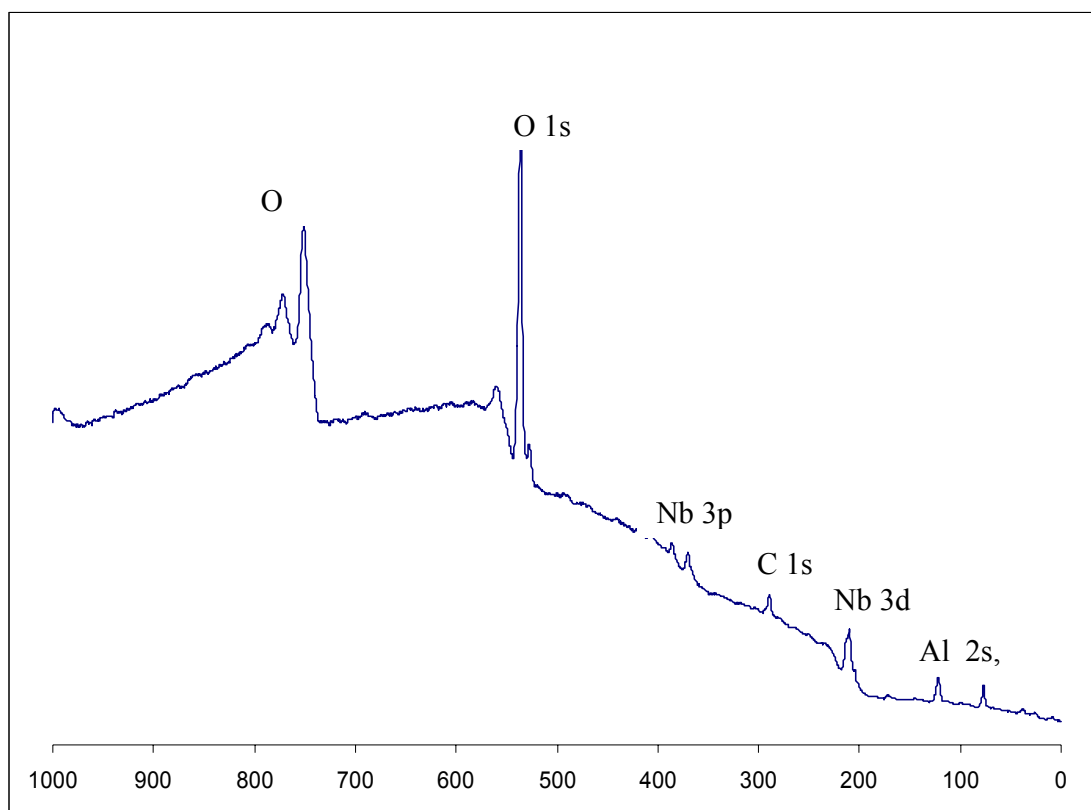
Although there are no reports of Nb ALD, thin films of a related superconducting material, NbN, have been prepared by ALD[6-8]. The study of the surfaces and morphology of ultrahigh purity Nb for use in SCRF cavities has been a recent active area of investigation.[9-14] These recent studies demonstrate that surface and interface segregation are crucial properties of these materials for SCRF applications since dissipative behavior is limited in this case to the first few 100 nm's of the material. Moreover, preferential diffusion/segregation at grain boundary or in the near surface are phenomena leading to large inhomogeneity in the material selvedge. Vacuum annealing of the Nb surface leads to a surface equilibrium with surface oxidation from residual vacuum gases being balanced by diffusion of the niobium oxide into the bulk material.

In this manuscript, we report on the initial studies demonstrating that ALD can be used to replace the chemically unconstrained Niobia dielectric layer with a stable line oxide (alumina), thus stabilizing the substrate surface. Initial temperature studies in air demonstrate that the alumina-stabilized surfaces do not show the oxide growth characterizing uncoated Nb metal.

### Experimental

The ALD films were deposited in a custom viscous flow reactor[15]. Ultrahigh purity nitrogen (99.999%) carrier gas was used at a mass flow rate of 360 sccm and a pressure of 1 Torr. Metal oxide films were deposited by ALD using alternating exposures to TMA/H<sub>2</sub>O to deposit films of Al<sub>2</sub>O<sub>3</sub>. The ALD timing sequences can be expressed as t<sub>1</sub>-t<sub>2</sub>-t<sub>3</sub>-t<sub>4</sub> where t<sub>1</sub> is the exposure time for the first precursor, t<sub>2</sub> is the purge time following the first exposure, t<sub>3</sub> is the exposure time for the second precursor, t<sub>4</sub> is the purge time following the exposure to the second precursor and all units are given in seconds (s). Typical timings for these depositions were 1-5-1-5. The deposition temperatures were kept at 150° C to limit Nb surface changes typically observed at temperatures above 150° C.

Nb coupons were prepared using ultrapure Nb metal which was polished and electrochemically etched following standard SCRF recipes to produce smooth



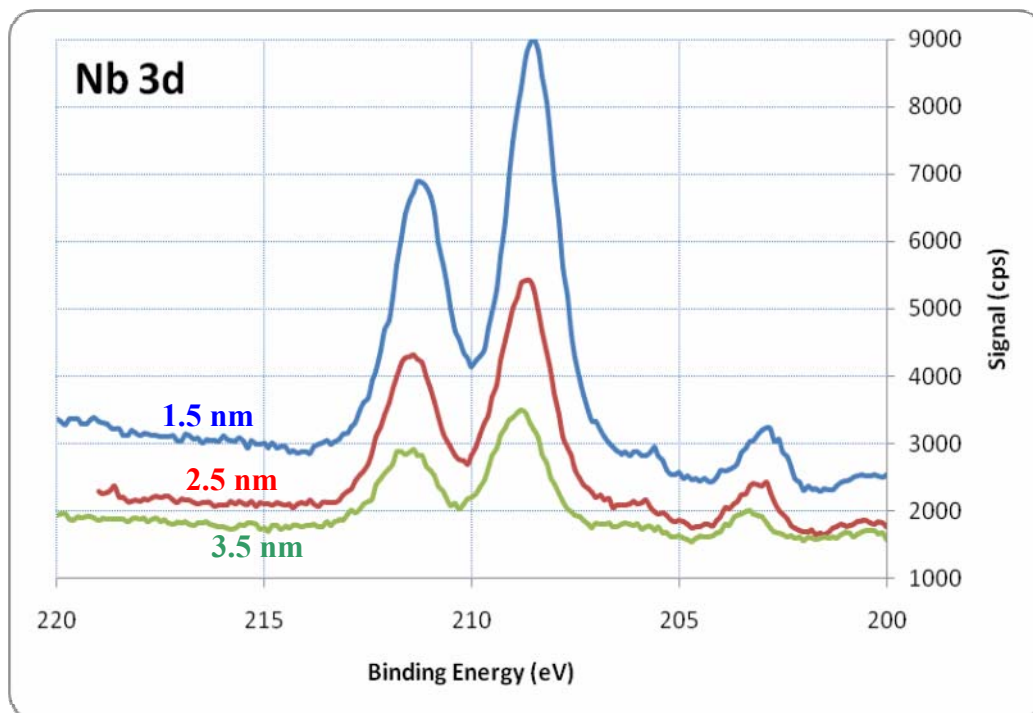
**Figure 1:** XPS survey of 2.5nm Al<sub>2</sub>O<sub>3</sub> film, showing the relative intensities of the elements present. The Al<sub>2</sub>O<sub>3</sub> was deposited using 20 cycles of trimethylaluminum (TMA) and water at 150°C. Alumina thickness was determined by spectroscopic ellipsometry on a silicon witness sample. Electron pass energy in eV is displayed on the x-axis. The Y axis is signal in arbitrary units.

surfaces.[14] A final HF etch was performed just prior to inserting the Nb coupons into the ALD reactor. The coupons were subsequently analyzed using X-ray photoelectron spectroscopy (XPS) and spectroscopic ellipsometry.

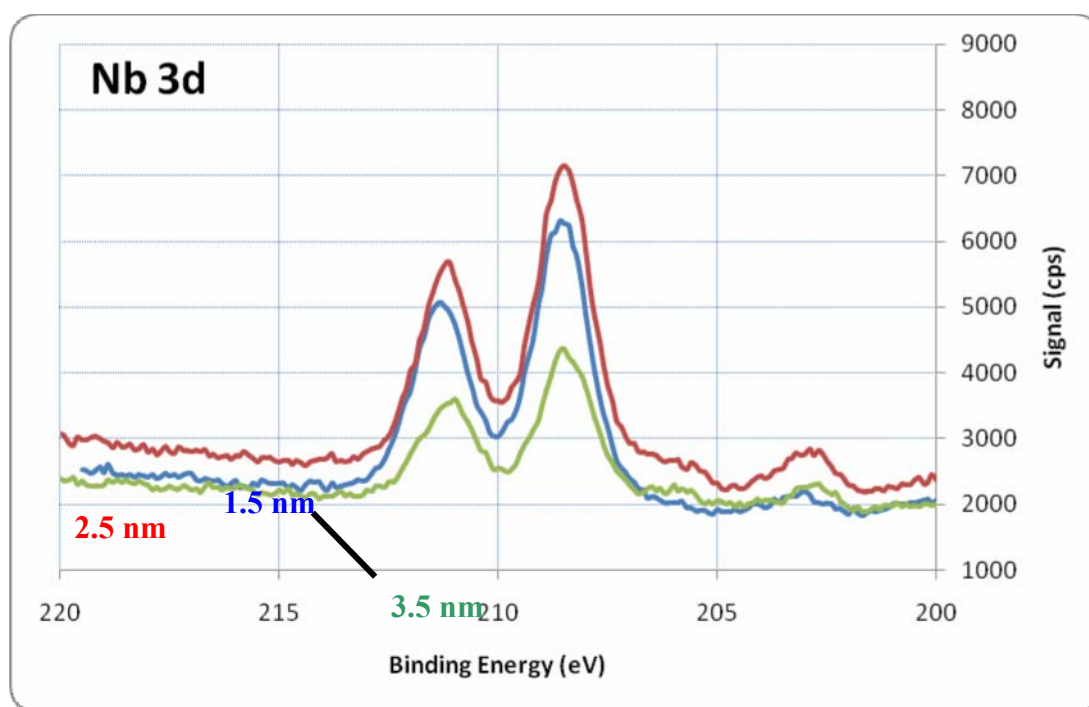
A typical XPS spectrum of the  $\text{Al}_2\text{O}_3$  film deposited on the Nb coupons is shown in **Fig.1**. Clearly evident are the Al lines associated with the ALD  $\text{Al}_2\text{O}_3$  film. The O peaks are a mixture of signals resulting from O bound to both Al and Nb due to the large escape depth of the O 1s electrons. The Nb oxygen peaks result from an inability to remove the oxide completely from the Nb surface before alumina growth in the ALD reactor. The major impurity is a small amount (<10%) of C. The carbon impurity may result from decomposition of the TMA on the Nb surface, or from atmospheric contamination during sample transfer from the ALD reactor into the XPS analysis system.

## Results and Discussion

Alumina films can easily be synthesized on the Nb coupons. Ellipsometry demonstrates that the growth rate is similar to that observed on Si samples. **Fig. 2** is a high resolution XPS spectrum of the Nb 3d region following deposition of  $\text{Al}_2\text{O}_3$  films of three different thicknesses. Alumina thickness as determined by spectroscopic ellipsometry is from top to bottom curve 1.5 (top curve), 2.5 (middle curve) and 3.5 nm (bottom curve), respectively. The prominent peaks at 208 and 211 eV are the  $3d_{5/2}$  and  $3d_{3/2}$  lines for Nb in the +5 oxidation state resulting from  $\text{Nb}_2\text{O}_5$ . The smaller peaks at 203 and 206 eV are the  $3d_{5/2}$  and  $3d_{3/2}$  lines for Nb metal. As expected, the Nb signal is screened by the increasingly thicker alumina over-layers. Importantly, the relative peak



**Figure 2:** Nb 3d core levels attenuated by progressively thicker coverage of  $\text{Al}_2\text{O}_3$  films grown by Atomic Layer Deposition at  $150^\circ\text{C}$ . Alumina thickness as determined by spectroscopic ellipsometry is from top to bottom curve 1.5, 2.5 and 3.5 nm, respectively.



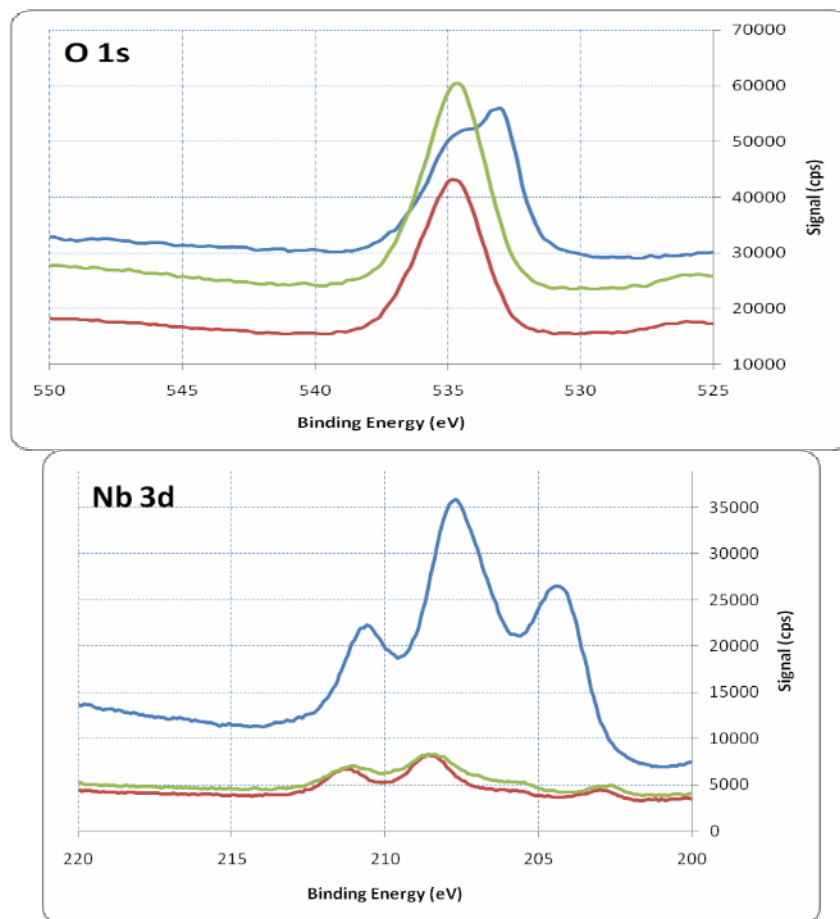
**Figure 3:** Niobium core levels for the same films as in figure 2, after air oxidation for 20 hours at 200°C. Initial alumina thickness as determined by spectroscopic ellipsometry indicated in boxes (1.5-3.5nm).

heights of the Nb 3d lines are not substantially affected by the deposition. This indicates that the Nb substrate is not further oxidized during the alumina deposition process. In fact, careful analysis of the relative peak heights indicates a slight reduction of the underlying Nb oxide, indicating a partial reduction of the  $\text{Nb}_2\text{O}_5$  by the TMA or the  $\text{Al}_2\text{O}_3$ .

A test of the “capping” ability of the alumina films is demonstrated in **Fig. 3**. Here the three coupons coated in **Fig. 2** are subjected to extensive (20 hour) air oxidation at 200°C. It is clear from the Nb 3d spectra that only the 1.5 nm film treated coupon experiences further oxidation during this process. Remarkably, the 2.5 and 3.5 nm thick alumina layers seem to completely prevent further oxidation of the underlying Nb substrate.

A comparison of the 1.5 nm alumina films air oxidation behavior (blue curve; **Fig. 3**) with that of a pristine Nb coupon treated to a similar air oxidation (blue curve; **Fig. 4**) shows that even this relatively thin alumina layer is effective in suppressing further Nb oxidation. The relatively small oxidation rate is possibly indicative of point failures in the coating rather than oxygen diffusion through the film.

These positive results were confirmed on a fourth coated Nb sample in **Fig. 4**. Here a 3.5 nm alumina film was grown on one of two identical Nb coupons. The coupons were then both subjected to 20 hrs of air oxidation at 200°C. High resolution XPS scans were then conducted on the uncoated samples before oxidation (shown in green), on the oxidized coated (shown in red) and the air oxidized uncoated sample (shown in blue). Both coupons showed significant oxidation following the standard electropolish and HF etch described in the experimental section. After oxidation, the uncoated sample displays much broader O 1s and Nb 3d lines indicative of oxidation with a broad range of suboxides. The coated sample in contrast is essentially unchanged.



**Figure 4:** Oxygen and Niobium core levels comparing a pristine Nb sample (No ALD, topmost curve) that has been air oxidized (20h at 200°C) to a sample that has been ALD coated with 3.5nm  $\text{Al}_2\text{O}_3$  (lowest curve) and then similarly oxidized (middle curve). ALD coating prevents growth of Nb mixed oxides.

## Conclusions

We have demonstrated the use of TMA and water to produce alumina on Nb substrates can cap the Nb substrate preventing further oxidation. This result is encouraging for ALD's application to SCRF accelerating cavity structures which require stable atomically abrupt dielectric boundaries.

## Acknowledgments

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